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THERMALLY STABLE ELECTROLYTES FOR RECHARGEABLE  
LITHIUM BATTERIES - PHASE II

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Covering the Period January 1, 1989 - August 31, 1989

Submitted by

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## ABSTRACT

During the second year of research under NASA SBIR Contract NAS7-967, Covalent Associates and NASA contract monitors at the Jet Propulsion Laboratory agreed to perform an evaluation of the three best electrolytes developed during Phase II. Due to the extensive period of time required to collect meaningful cycling data, we realized the study would extend well beyond the original formal end of the Phase II program (August 31, 1988). The substitution of this effort in lieu of an earlier proposed 20-cell final deliverable is formally documented in Modification No. 1 of Contract NAS7-967 as Task 7.

This Addendum contains the results of the cycling studies performed at Covalent Associates. In addition, sealed ampoules of each of these three electrolytes were delivered to the Jet Propulsion Laboratory Electrochemical Power Group. Their concurrent evaluation in a different test vehicle has also been recently concluded and their results are also summarized herein.

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## OBJECTIVE

During Phase II a host of electrolytes were developed and compared in a standardized 260 mAh  $TiS_2$  test vehicle. While this procedure identified several potentially important electrolytes, their capabilities remained to be determined in electrochemical cells which would more surely achieve the NASA goal of greater than 500 50% depth-of-discharge (DOD) cycles. We believed the Li Figures of Merit were being compromised by overly thick cathodes, which may develop concentration gradients and trap degradation products. Therefore, we built a test vehicle with thinner cathodes and a higher Li/ $TiS_2$  ratio. In so doing, we expected to achieve better Li utilization and a significantly greater number of useful discharges.

Concurrently, the JPL team subjected the electrolytes to 100% DOD cycling in their standard test vehicle with the primary goal of verifying state-of-the-art Li utilization, i.e., high FOMs.

The overall goal of this Phase II effort was to develop the technology base needed to fabricate high energy density/high cycle life rechargeable Li cells which will fly on future NASA missions. Based upon the data presented in the Final Report and in this Addendum, we believe that this goal has been achieved.

## EXPERIMENTAL

Below are the specifications for the Covalent Associates test vehicle used in this set of experiments:

Discharge = 2 mA/cm<sup>2</sup>, Charge = 1 mA/cm<sup>2</sup>

15 minute rests after charge and discharge

Voltage limits 2.7V - 1.6V

FOM cut off defined as 30% DOD

Cycling will be at 50% DOD at theoretical TiS<sub>2</sub> capacity

Li will be 10 mil, 1 Ah/cell

TiS<sub>2</sub> will be 6.5 mAh/cm<sup>2</sup>/cycling side and 15 mil thick in the cathodes fabricated at Covalent (8 w/o Teflon, 8 w/o Shawinigan carbon black)

Electrodes will be 1" x 1 1/2"

Total TiS<sub>2</sub> capacity will be 130 mAh

Li/TiS<sub>2</sub> = 7.7/1

5 ml of electrolyte/cell

LiAsF<sub>6</sub> is Lithco tetrakisacetonitrile desolvate process (Lot 8801192H)

The JPL research group used their standard spiral-wound test vehicle (1) with EPDM cathode binder and an approximate cathode capacity of 150 mAh and Li capacity of 1 Ah. The cells were cycled initially to full 100% DOD cycles. Breakpoint values are defined as the cycle number when 40% of the original capacity was achievable. Current densities were 2 mA/cm<sup>2</sup> (discharge) and 1 mA/cm<sup>2</sup> (charge).

The electrolytes prepared in the temperature range of -20 to +10°C were:

- 1) 1.5M LiAsF<sub>6</sub>/THF (Li-Hg)/0.7 v/o 2-MeF/18Crown6/KOH
- 2) 1.5M LiAsF<sub>6</sub> 50-50 v/o THF + 2-MeTHF/0.7 v/o 2-MeF/KOH
- 3) 1.5M LiAsF<sub>6</sub>/DIOX (Li-Hg)/0.7 v/o 2-MeF/18Crown6/KOH

## RESULTS AND DISCUSSION

Tables 1 and 2 summarize the results of the full cell cycling studies at Covalent Associates and JPL.

TABLE 1  
Summary of Final Cycling Program Results at Covalent

Electrolyte	Current Densities	Cell Number	50% Cycles	FOM
<u>1.5M LiAsF<sub>6</sub> in:</u>	<u>D/C (mA/cm<sup>2</sup>)</u>	---	---	---
Blend 50/KOH/2-MeF	2/1	026-124-13	542/581	39.3
		026-124-14	104	14.4
	1/0.5	026-125-37	401	32.6
		026-125-38	600	>41*
THF/18Crown6/KOH/2-MeF	2/1	026-127-74	415/531	36.3
		026-127-75	48	4.7
	1/0.5	026-127-62	340	23.2
		026-127-63	321	23.3
DIOX/18Crown6/KOH/2-MeF	2/1	026-128-98	67	7.4
		026-128-99	35	4.7
	1/0.5	026-128-86	232	15.3
		026-128-87	125	13.5

\*Still cycling at 48% DOD at cycle 615

TABLE 2  
Summary of Cycling Results at JPL

Electrolyte	Total Cycles 100% DOD initial 40% DOD Cut-Off	FOM
1.5M LiAsF <sub>6</sub> in: Blend 50/KOH/2-MeF	320*	39
	320	39
THF/18Crown6/KOH/2-MeF	300	36
	300	36
DIOX/18Crown6/KOH/2-MeF	300	34
	250	24

\*Average capacity per cycle = 120 mAh

Prior to these studies, Covalent Associates' best Li FOMs in cells with thick (260 mAh) cathodes were in the range of 28 to 30. Our superior FOMs of 39 to 40 from the redesigned, thinner cathode (130 mAh) test vehicle clearly confirm that electrolytes now exist which can fulfill the NASA goal of greater than 500 50% DOD quality discharges. By adjusting the engineering parameters we increased the Li efficiency by 33 percent.

The JPL team has confirmed our findings by achieving surprisingly similar best FOMs with the Blend 50 and THF-based electrolytes. Additionally, they also achieved what we believe is the best ever reported Li FOM with an LiAsF<sub>6</sub>/DIOX-based system. Both groups found the Blend 50 and THF systems to be somewhat better than DIOX. We suspect that a greatly reduced but steady low level of DIOX polymerization may still proceed on the surface of the TiS<sub>2</sub> crystallites and within the bulk electrolyte, thereby contributing to the premature capacity fade relative to the THF and Blend 50 systems.

As determined at JPL, microcalorimetry of filled cells with all three electrolytes favorably indicates low heat evolution during storage on open-circuit. This is a necessary prerequisite for a battery to have a long shelf life and is particularly important for multi-year NASA missions.

Figures 1 through 6 collect the voltages as a function of cycle number for the cells fabricated at Covalent. All are at the 50% DOD endpoint voltage except Figure 3A which complements Figure 3B by comparing 25% DOD voltages with 50% DOD voltages (*vida infra*).

Despite the presence of identical electrolyte in duplicate cells, several duplicate cells exhibited substantial variance from each other. We attribute this to a combination of cell to cell hardware differences and the complicated morphologies inherent in Li electrodeposition through subsequent charge cycles.

Figures 1 and 2 depict endpoint plots for the Blend 50 cells at  $2\text{mA/cm}^2$  and  $1\text{mA/cm}^2$  discharge rates, respectively. The best results in each case yielded FOMs of 40 or so and about 600 cycles.

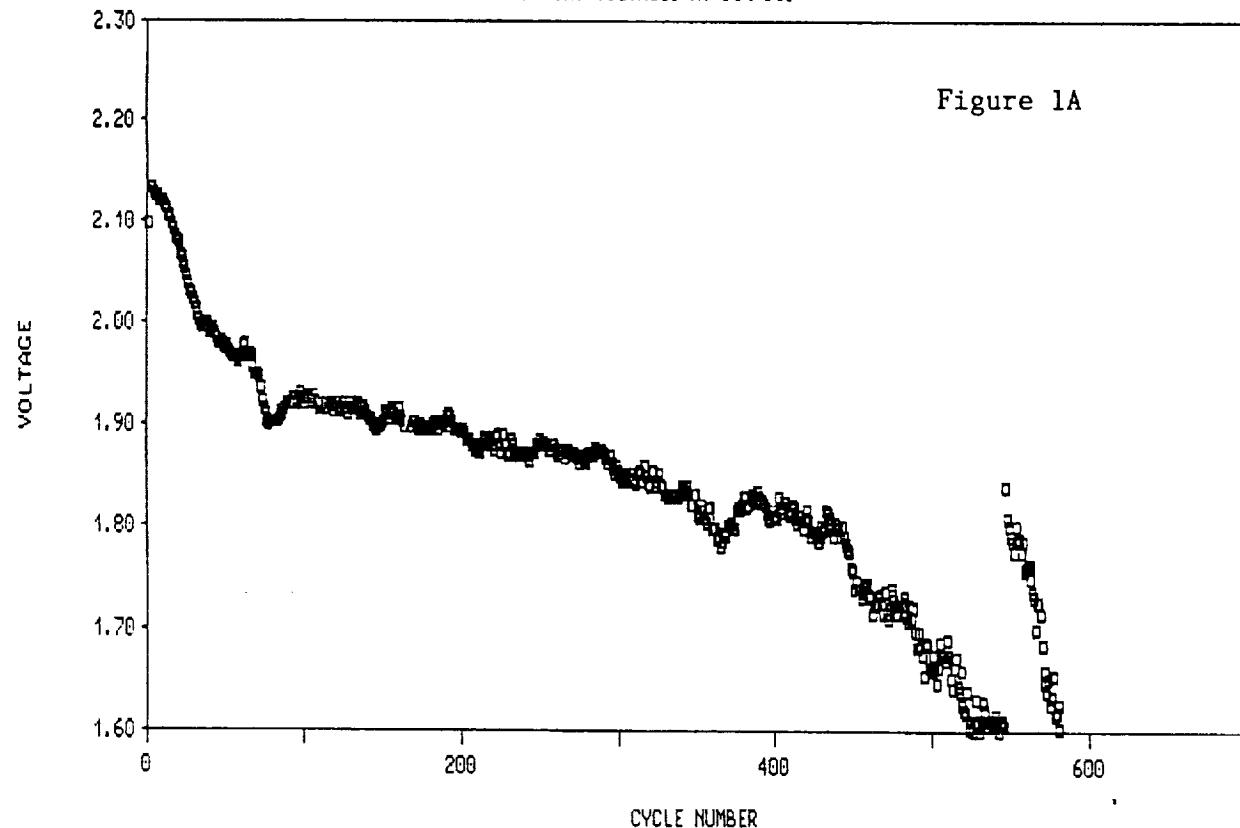
In Figures 3A and 3B, the midpoint (25% DOD) and endpoint voltages for the  $2\text{mA/cm}^2$  discharge rate are plotted for a cell containing the THF-based electrolyte. This cell's capacity became limited to 50% at cycle 415. A subsequent 50% reduction in discharge and charge currents afforded a total of about 531 50% DOD cycles. Figure 3A, the 25% DOD voltage profile, is included to demonstrate that during the early portion of the discharge the voltage remains near 2.1V even as the voltage drops faster deeper in the discharge.

Figures 4A and 4B show very repeatable Li FOMs of 23.2 and 23.3 at the lower,  $1\text{mA/cm}^2$ , discharge rate. A review of all the THF and Blend 50 results shows little apparent difference in cycling efficiency at the two different discharge rates.

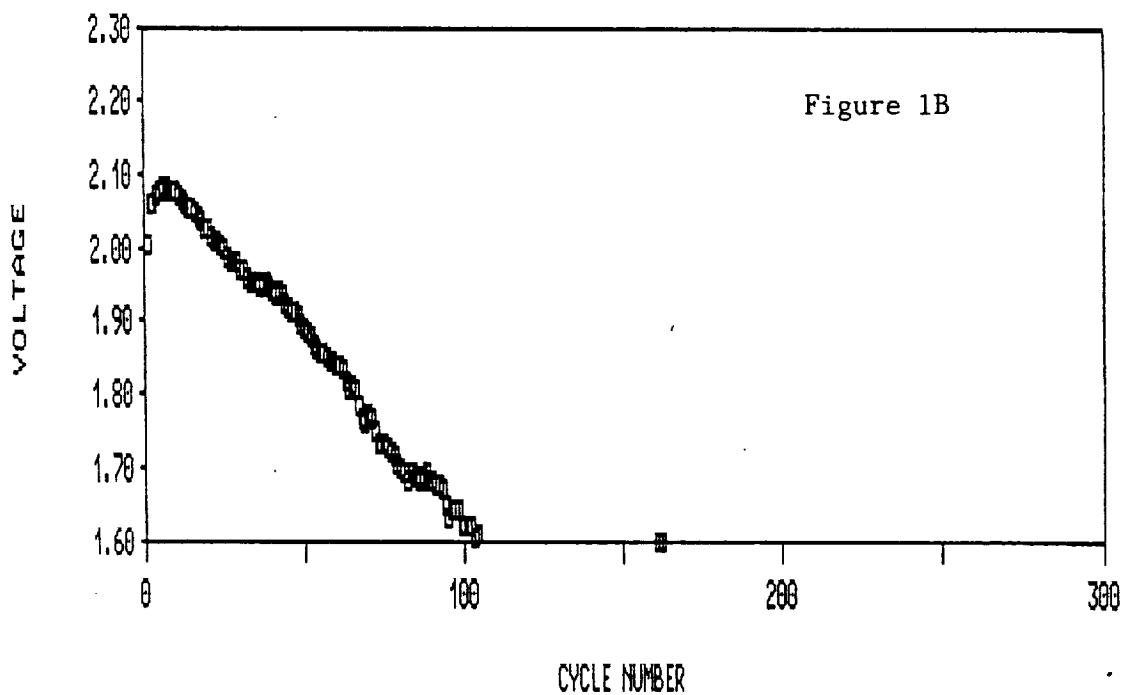
Finally, DIOX cycling results are shown in Figures 5 and 6. These results are inferior to both other electrolytes in this series; however, we obtained significantly better results during the second year of Phase II with our thicker cathodes. The major difference between the experiments is that during Phase II we used  $\text{TiS}_2$  which had been pretreated by immersion in THF saturated with KOH.

This procedure eliminates residual acidic impurities in the  $\text{TiS}_2$  prior to exposure to the electrolyte. It is quite likely that KOH treated  $\text{TiS}_2$  used in the current test vehicle would afford comparable FOMs, as was the case in the second year of Phase II.

CELL 026-124-13  
ENDPOINT VOLTAGES AT 50% DOD

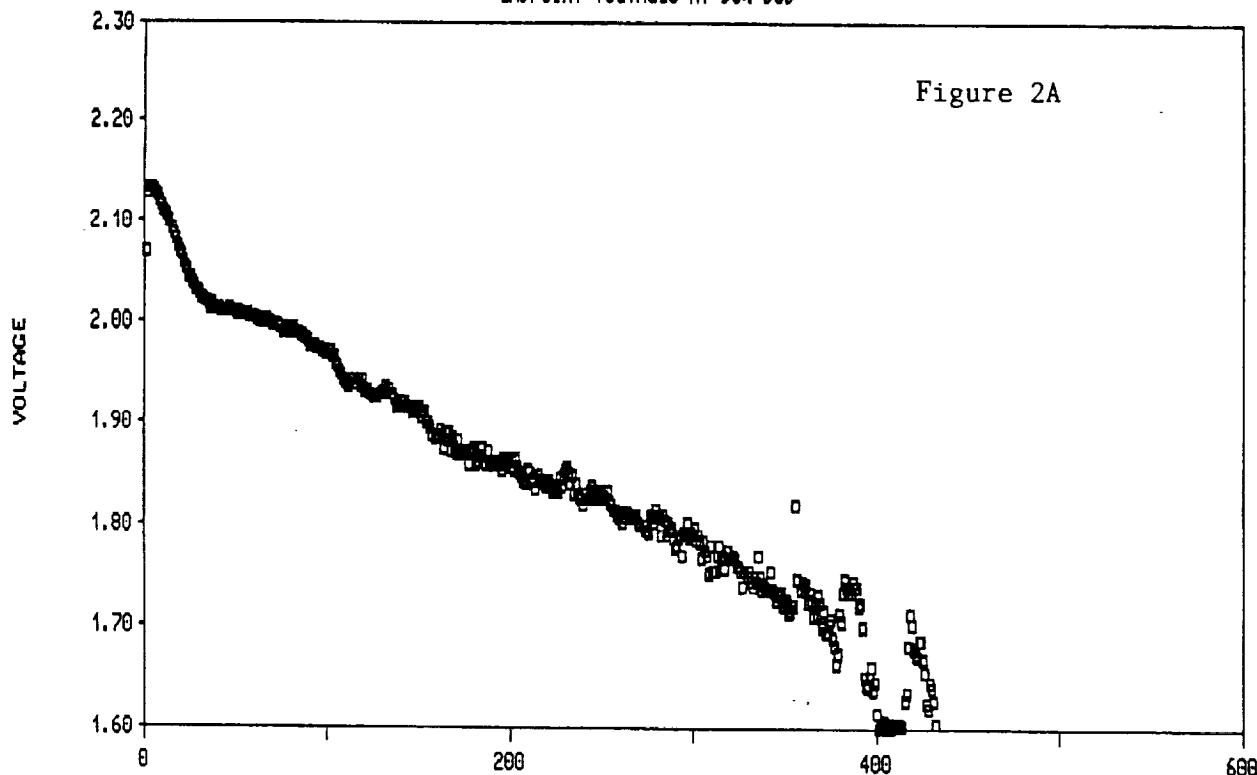


CELL 026-124-14  
ENDPOINT VOLTAGES AT 50% DOD

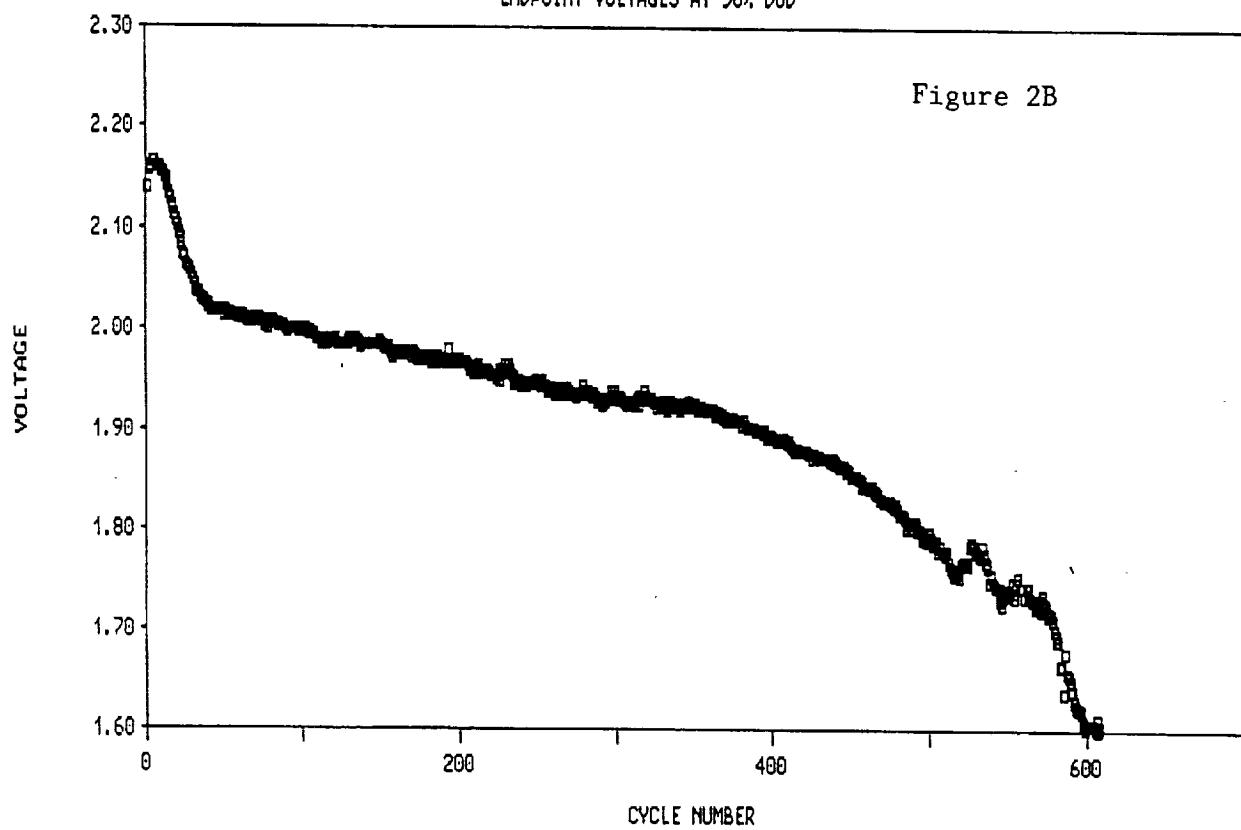


Figures 1A (Top) and 1B (Bottom): Endpoint Voltage Profile for 1.5M LiAsF<sub>6</sub>/  
Blend 50/2-MeF/KOH Electrolyte Discharged at 2mA/cm<sup>2</sup>.

CELL 026-125-37  
ENDPOINT VOLTAGES AT 50% DOD

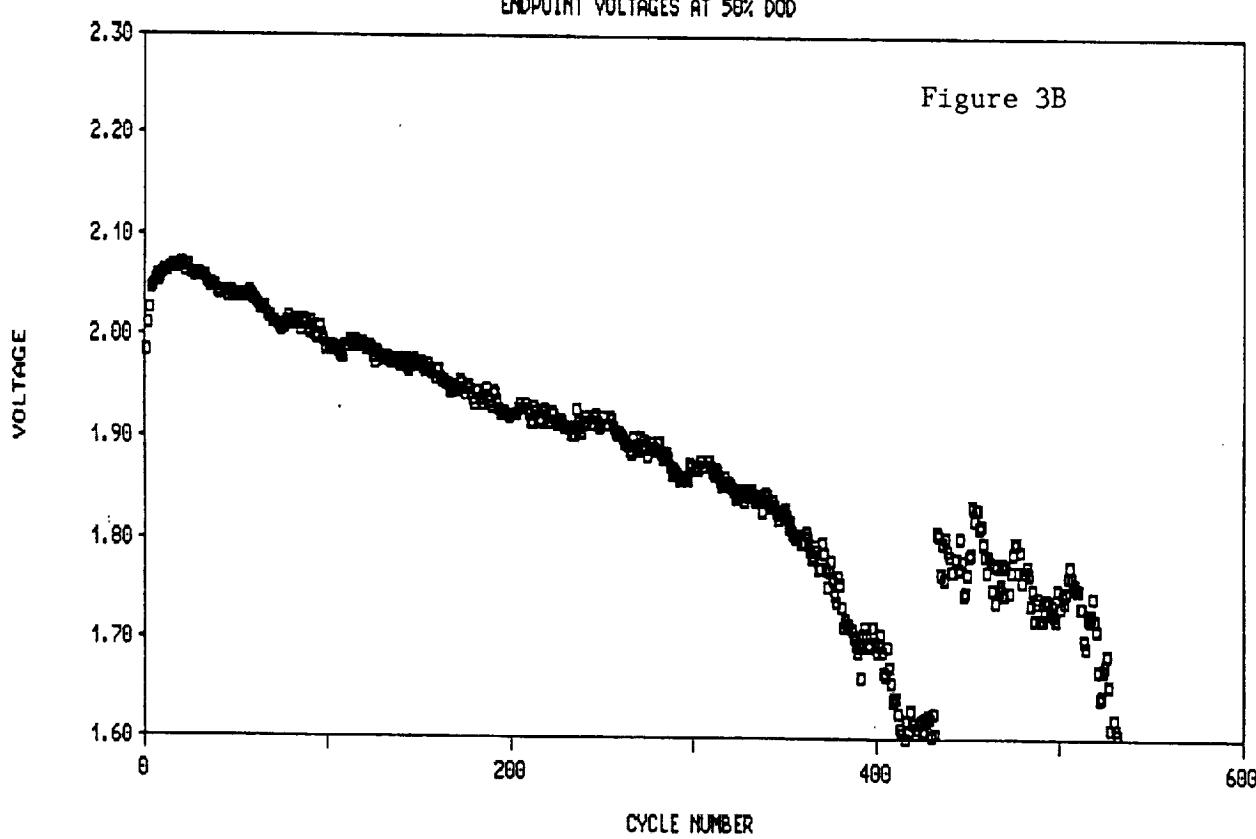
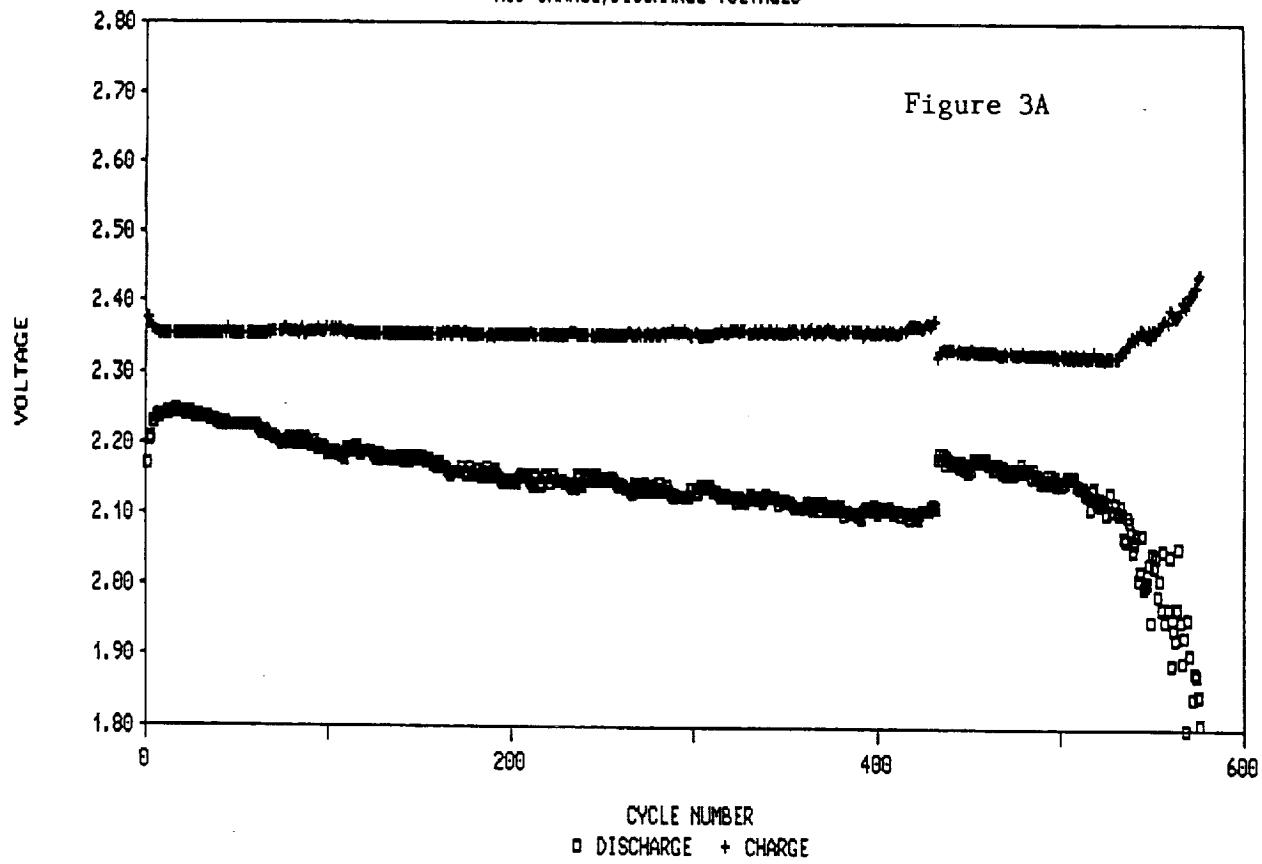


CELL 026-125-38  
ENDPOINT VOLTAGES AT 50% DOD



Figures 2A and 2B: Endpoint Voltage Profile for 1.5M LiAsF<sub>6</sub>/Blend 50/2-MeF/KOH Electrolyte Discharged at 1mA/cm<sup>2</sup>.

CELL 026-127-74  
MID-CHARGE/DISCHARGE VOLTAGES



Figures 3A and 3B: Endpoint Voltage Profiles at 25% DOD (Top) and 50% DOD (Bottom) for 1.5M LiAsF<sub>6</sub>/THF/2-MeF/18Crown6/KOH Electrolyte Discharged at 2mA/cm<sup>2</sup>.

CELL 026-127-62  
ENDPOINT VOLTAGES AT 50% DOD

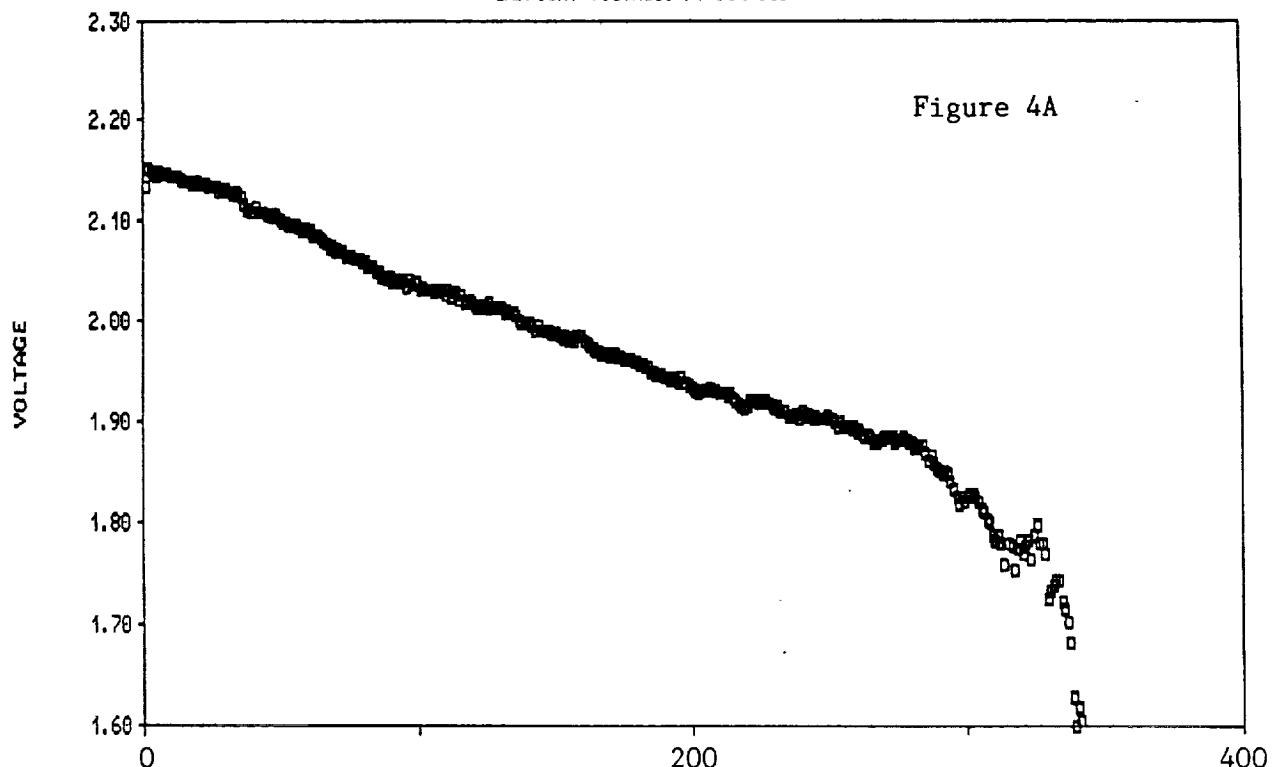


Figure 4A

CELL 026-127-63  
ENDPOINT VOLTAGES AT 50% DOD

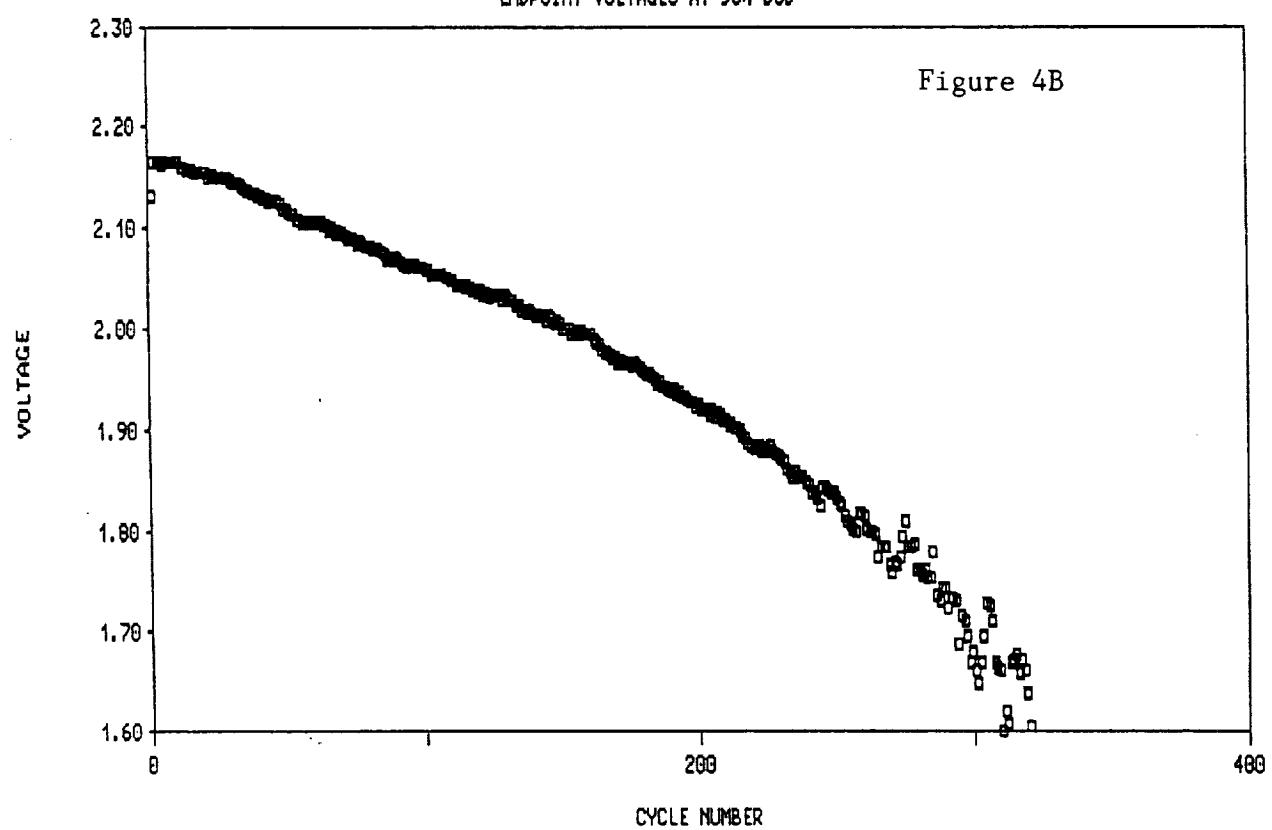
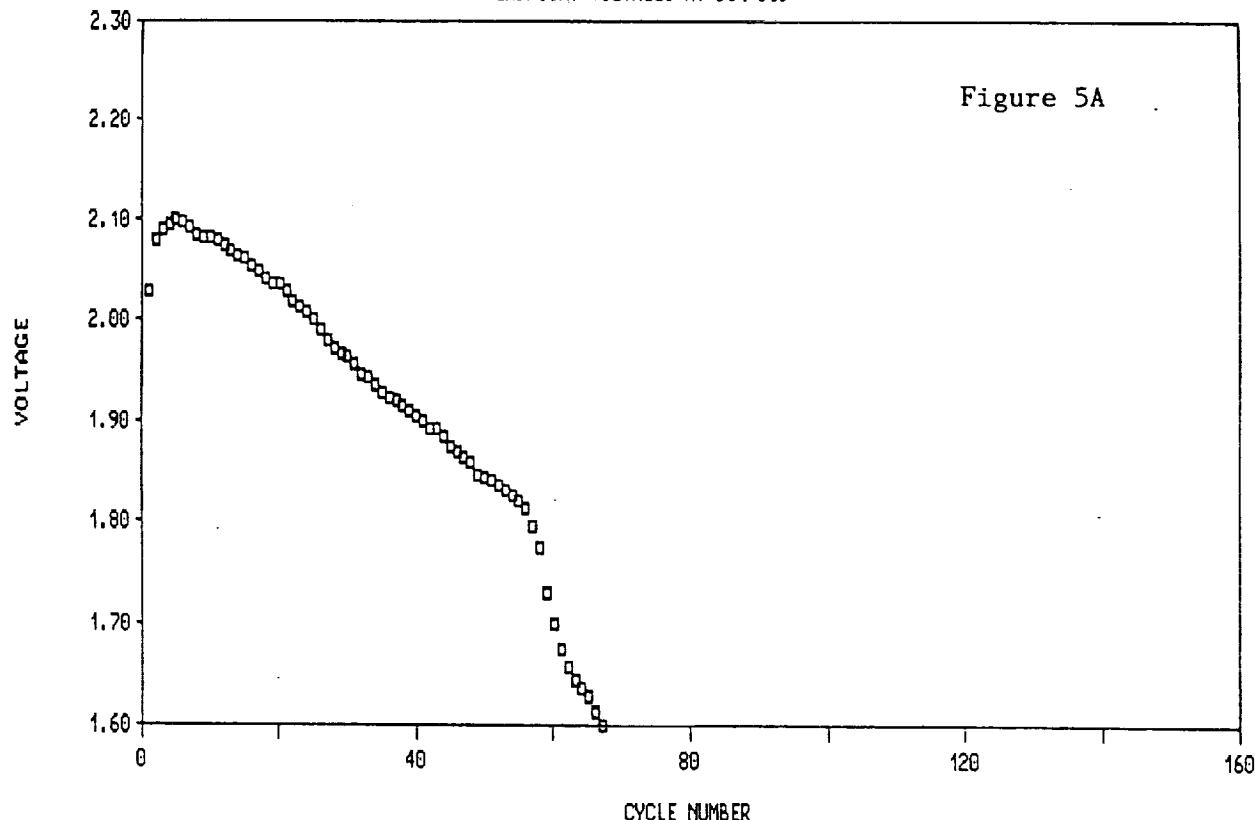


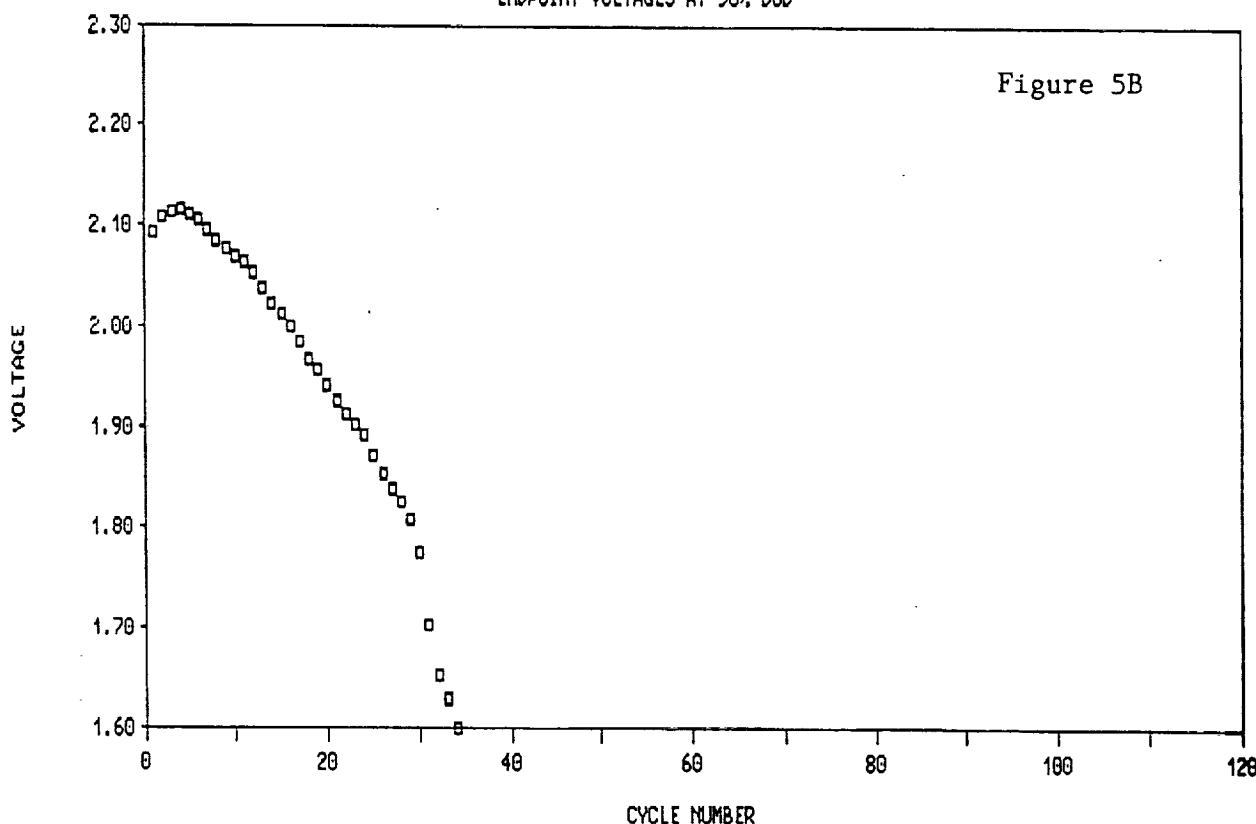
Figure 4B

Figures 4A and 4B: Endpoint Voltage Profiles for 1.5M LiAsF<sub>6</sub>/THF/2-MeF/18Crown6/KOH Electrolytes Discharged at 1mA/cm<sup>2</sup>.

CELL 026-128-98  
ENDPOINT VOLTAGES AT 50% DOD

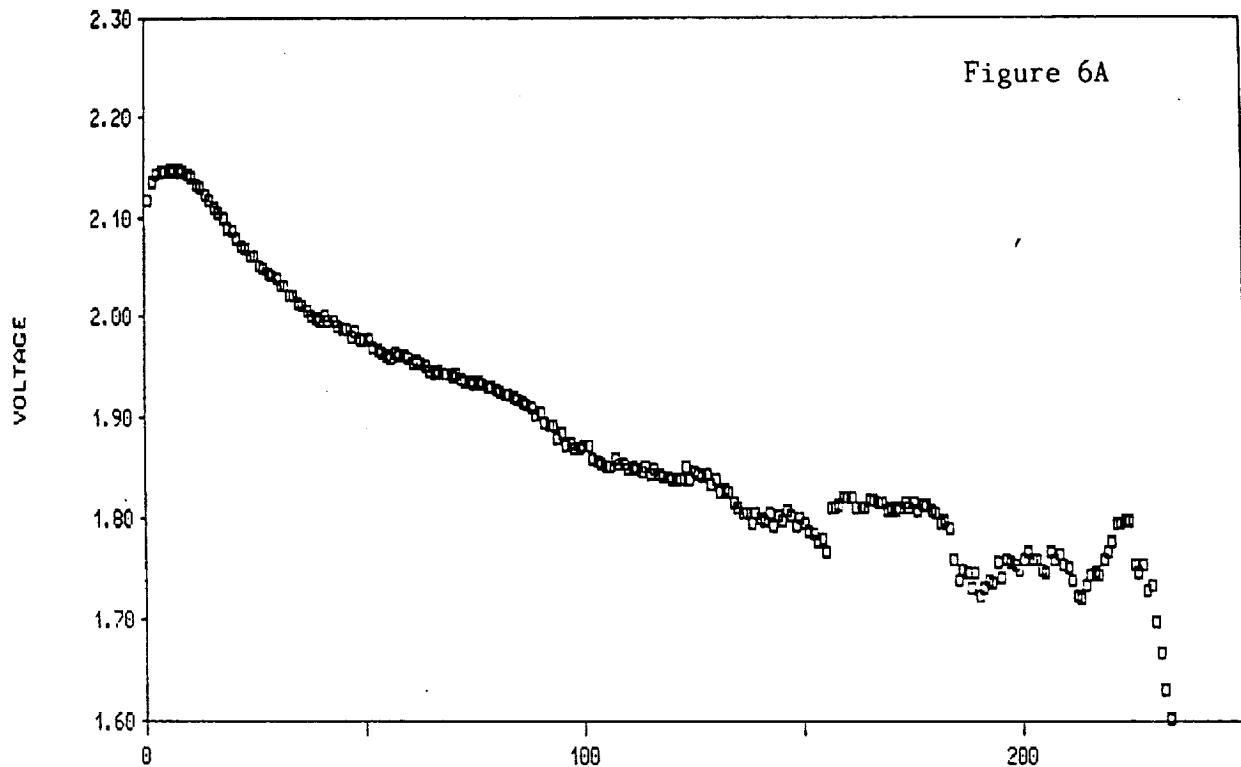


CELL 026-128-99  
ENDPOINT VOLTAGES AT 50% DOD

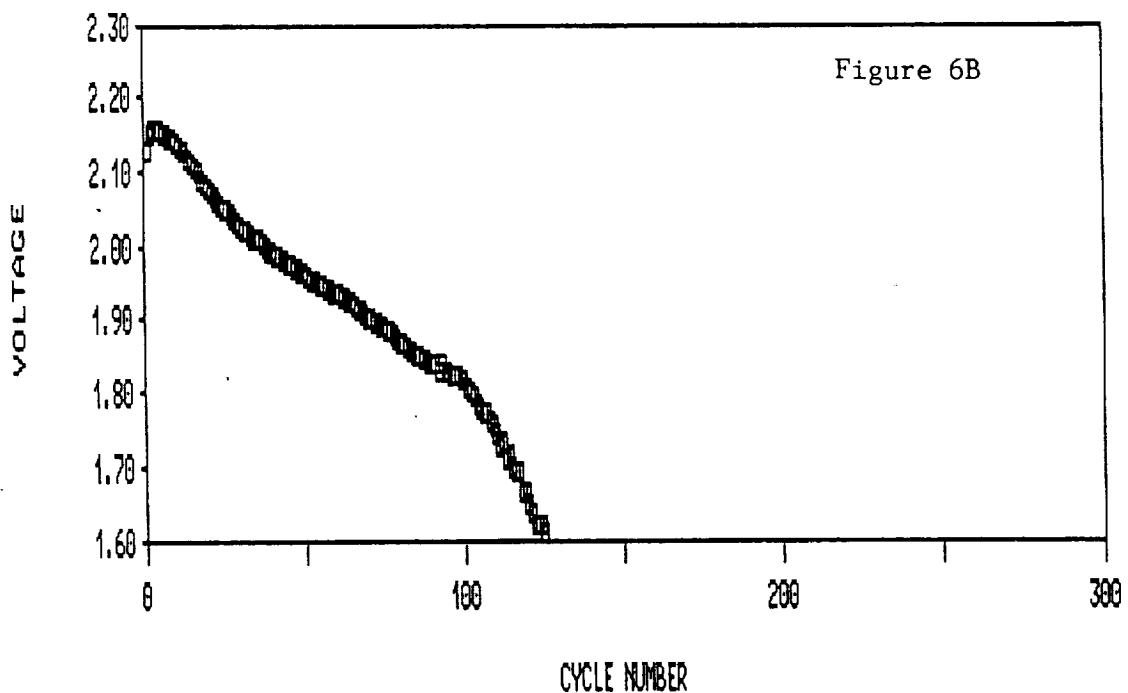


Figures 5A and 5B: Endpoint Voltage Profiles for 1.5M LiAsF<sub>6</sub> /DIOX/2-MeF/18Crown6/  
KOH Electrolytes Discharged at 2mA/cm<sup>2</sup>.

CELL 026-128-86  
ENDPOINT VOLTAGES AT 50% DOD



CELL 026-128-87  
ENDPOINT VOLTAGES AT 50% DOD



Figures 6A and 6B: Endpoint Voltage Profiles for 1.5M LiAsF<sub>6</sub>/DIOX/2-MeF/18Crown6/KOH Electrolytes Discharged at 1mA/cm<sup>2</sup>.

#### Evaluations by Outside Vendors:

In the last year, Covalent Associates has made small samples of the THF and Blend 50-based electrolytes available to potential manufacturers of Li/TiS<sub>2</sub> batteries.

A series of cycling studies at Eveready Battery Company (Cleveland, OH) concluded that the Covalent modified Blend 50 electrolyte afforded significantly higher cathode utilization than other electrolytes with which they were familiar when cycled at 60% DOD and 1mA/cm<sup>2</sup> discharge-0.5mA/cm<sup>2</sup> charge rates. Li FOMs of 55.4 and 55.1 were achieved in duplicate cells. Cycling was halted at this time. However, one cell was still demonstrating a 1.9V endpoint. This indicates that substantial cycleability remained. A detailed summary of this set of experiments has been reviewed by the JPL Electrochemical Power Sources Group.

Additionally, a recent comparison of our improved Blend 50 and THF electrolytes at W. R. Grace (Columbia, MD) has been completed. They found that when compared with the Blend 50 electrolyte, our THF electrolyte afforded a reproducibly higher cathode utilization under relatively high rate discharge conditions.

#### CONCLUSION

With the development of these improved electrolytes, it is now feasible to build a rechargeable Li/TiS<sub>2</sub> battery capable of both good cycle life (>500 50% DOD) and improved rate capability (at least C/3). While improvements over present systems have been demonstrated and confirmed, further improvements are highly likely. These will come about by electrolyte component optimization (e.g., concentration/performance studies) and by further advances in cell engineering.

#### REFERENCE

1. D. Shen, S. Subbarao, F. Deligiannis, and G. Halpert in Proc. Symp. on Materials and Processes for Lithium Batteries, K. M. Abraham and B. B. Owens, eds, Vol. 89-4 (The Electrochemical Society, 1989), p. 223.